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Laboratory Procedure for the Gravimetric Determination of Carbon and Hydrogen in Solid Wastes (for Methods Manual)

Bureau of Solid Waste Management

1970

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Carbon and hydrogen are determined gravimetrically after combusting a weighed, dry, uniform sample in an atmosphere of oxygen with a closed system and fixing the combustion products in an absorption train. The procedure is designed to measure the total carbon and hydrogen in dry solid wastes samples.

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LABORATORY PROCEDURE FOR THE GRAVIMETRIC DETERMINATION OF CARBON AND HYDROGEN IN SOLID WASTES (FOR METHODS MANUAL)

A Division of Research and Development
Open-File Report (RS-03-68-17)

written by

Donald L. Wilson, Research Chemist

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service
Bureau of Solid Waste Management
1970

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DISCUSSION

Carbon and hydrogen are determined gravimetrically after (1) combusting a weighed, dry, uniform sample in an atmosphere of oxygen with a closed system and (2) fixing the combustion products in an absorption train (Figure 1.). The procedure (Figure 2.) is designed to measure the total carbon and hydrogen in dry solid wastes samples.

The 38-inch (1 1/2-inch O.D.) combustion tube, starting at a point 16 1/4 inches from the non-tapered end contains the following materials in the order named (Figure 3.): Special mixture of asbestos, platinized abestos, and aluminum oxide; lead chromate; asbestos; copper dioxide; asbestos; lead chromate; silver wool; lead dioxide; and silver wire. The plain abestos is employed

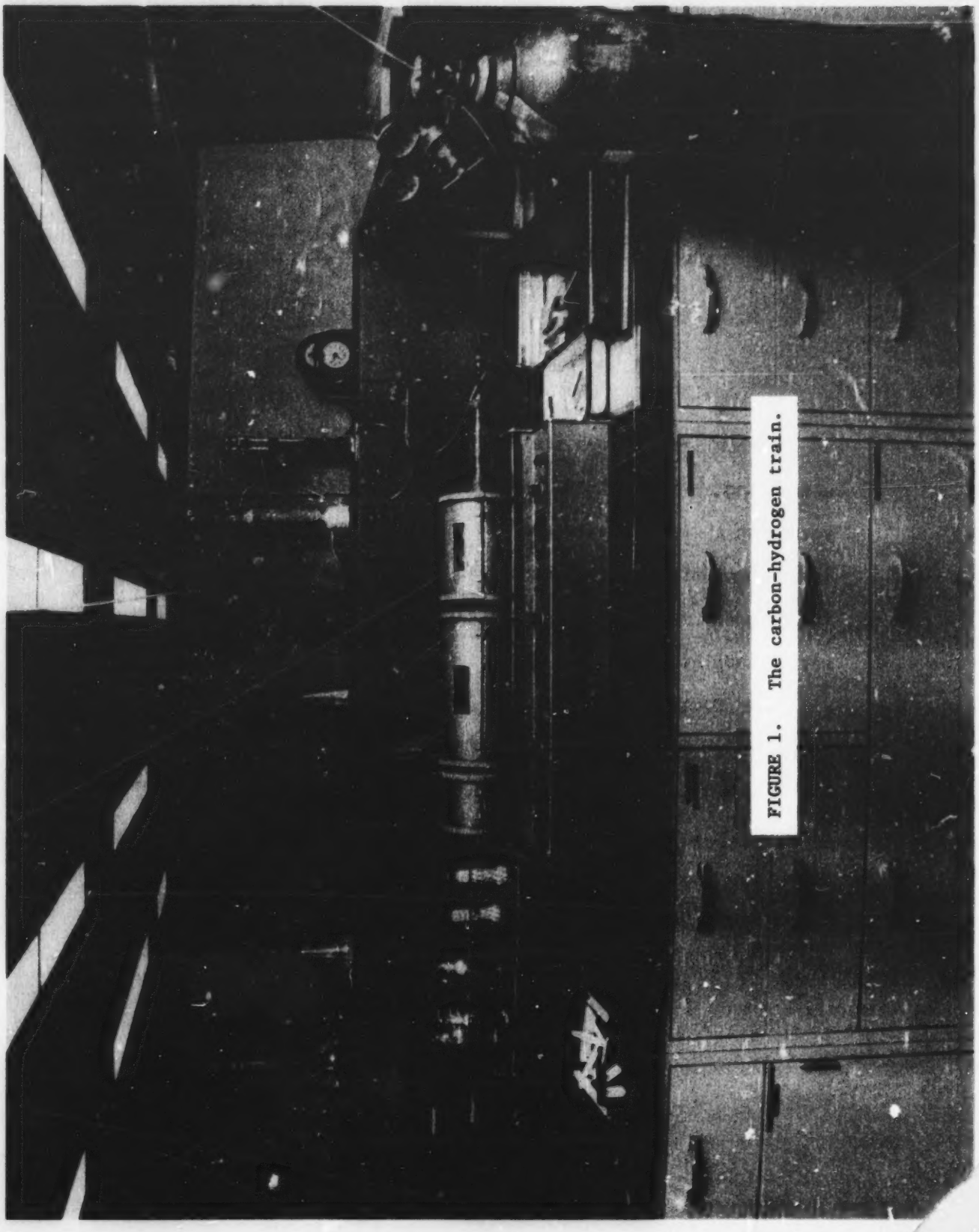

FIGURE 1. The carbon-hydrogen train.

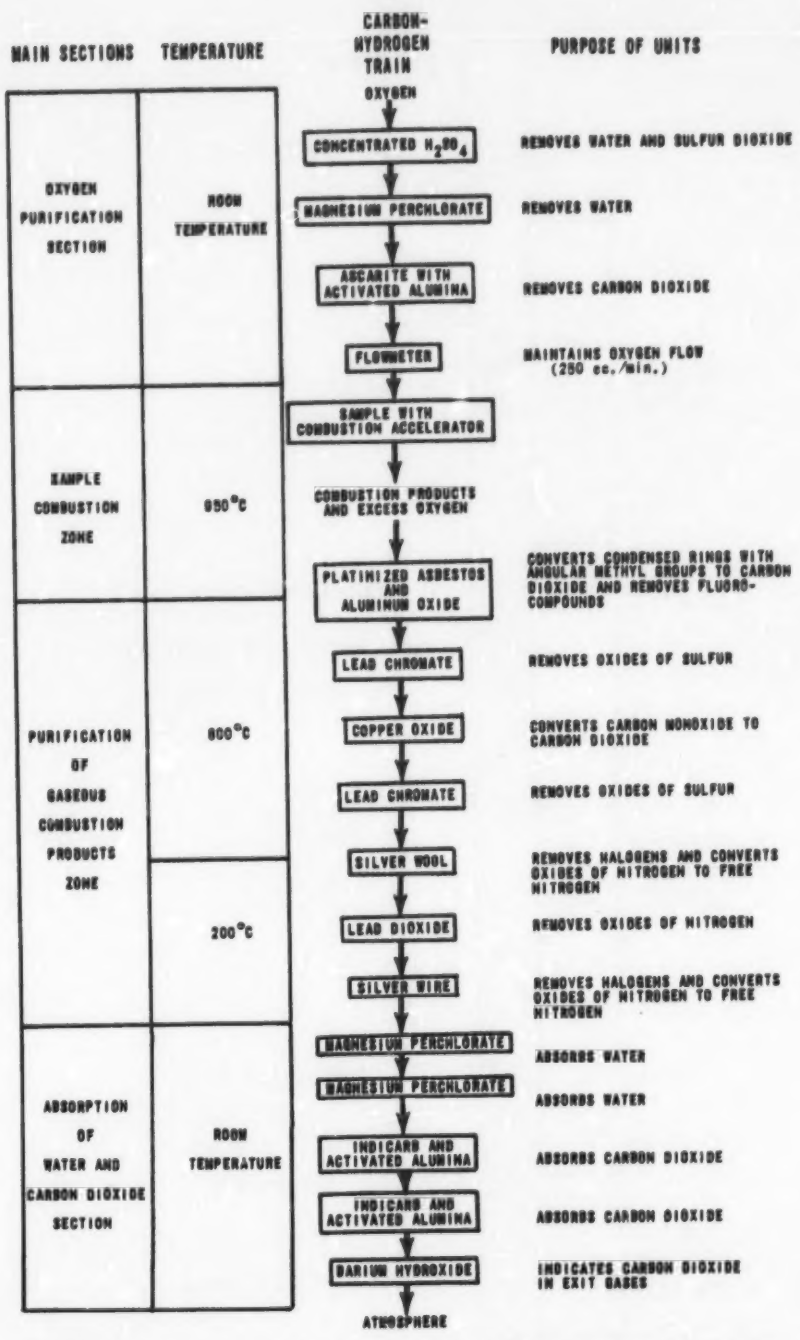

FIGURE 2. General outline of carbon-hydrogen train.

as a support between the materials in the tube. The platinized asbestos, located near the sample combustion area, assists in the combustion of condensed ring systems, particularly those containing an angular methyl group which may evolve as methane and thus escape complete combustion. Aluminum oxide is used to absorb fluorine from the diffusing gaseous combustion products while lead chromate oxidizes any SO_2 to SO_3 and, finally, to the non-volatile sulfate ($PbSO_4$). Copper oxide converts any carbon monoxide to carbon dioxide while lead dioxide retains the oxides of nitrogen as follows:

$$2NO + 2PbO_2 \xrightarrow{\Delta} Pb(NO_2)_2 \cdot PbO + 1/2\ O_2$$

$$2NO_2 + 2PbO_2 \xrightarrow{\Delta} Pb(NO_3)_2 + PbO + 1/2\ O_2$$

The sections of silver wire and silver wool, located near the tapered end of the combustion tube, absorb chlorine, bromine, and iodine from the gaseous combustion products before their diffusion from the combustion tube and into the magnesium perchlorate and Indicarb®, employed to absorb the water vapor and carbon dioxide gas respectively.

Samples containing (1) alkali or alkaline earths, as potash or calcium oxide, in the absence of sulfur or phosphorus or (2) phosphorus in the absence of alkali or alkaline earths can only be evaluated if an accelerator is added to the samples to insure complete combustion and conversion of all the carbon to carbon dioxide. Iron chips (carbon free) are used as the accelerator. The iron ignites and starts the exothermic combustion reactions before the sample reaches the final induced temperature of 950 C.

This method is applicable to raw garbage, compost, incinerator residue, and other dry, general wastes samples, which can have a carbon content of 0.5 to 83.0% and a hydrogen content of 0.01 to 7.80%. Samples containing appreciable amounts of arsenic, antimony, bismuth, and mercury should not be analyzed unless further modifications in the procedure are made, since these elements would quickly deteriorate the combustion tube packing.

Since hydrogen is analyzed as water, it is essential that all of the moisture be removed from the samples before they are analyzed. All samples must be re-dried no more than a few days before the analyses are performed.

APPARATUS

Requirements

1. Asbestos boards, 6 x 6 x 1/8 inches, 12 x 12 x 1/8 inches
2. Baffle, oxygen (Sargent #S-21787)*
3. Balance, analytical, 200g capacity, 0.1 mg readability
4. Barge, combustion, high purity nickel (Fisher #7-647)
5. Baskets, test tube, one size C, four size D (Fisher #14-966)
6. Boats, combustion, clay (Fisher #7-651) with covers (Fisher #7-652)
7. Boats, large, combustion, clay (Fisher #12-183N) with covers (Fisher #12-1835 N)
8. Bulbs, absorption, Nesbitt (for carbon dioxide)(4), (Fisher #7-515)
9. Bulbs, absorption, Stetser-Norton (for water)(2), (Fisher #7-565)
10. Charger-rake (Fisher #7-610)
11. Clamps, utility, three-prong grip (Fisher #5-768-10)
12. Desiccator cabinet (Fisher #8-645-5)
13. Erlenmeyer flask, two, 500 ml

*Product (or manufacturer) identification shown in this Method does not imply endorsement by the United States Public Health Service.

14. Furnace, modified, combustion, organic, "multiple unit," electric, tube type (Lindberg #123-T-S)
15. Furnace, muffle, operating temperature of 950 C
16. Glass tubing to fit two-hole stoppers
17. Gloves, lint-free
18. Inserter, sample (Dietert Co. #3452)
19. Jar, drying, 300 mm in height (Fisher #9-210)
20. Oxygen cylinder with (a) pressure regulator, adjustable from zero to ten pounds of pressure on the low pressure side and (b) needle-valve control
21. Pan, enameled (Fisher #9-017)
22. Pan, stainless steel, two, (Fisher #13-361, size D)
23. Rotameter, ends designed for tube connections, maintains an oxygen flow of 250 cc/min. (Ace Glass, Inc., "Rota-Kit," Tru-Taper #1, size 1A-15-1)
24. Stand, support, size A (Fisher #14-675)
25. Stopcock, glass, T-bore, 8 mm O.D. stems (Ace Glass, Inc. #8178)
26. Stopcock, hard rubber (Fisher #14-630)
27. Stoppers, two-hole, size #7
28. Timer (Fisher #6-662)
29. Tube, combustion, Vycor, 38 inches long, 1-1/4 inches I.D., 1-1/2 inches O.D., one end tapered to fit 3/16 inches I.D. rubber tubing [may use McDanel tube, 36 inches long (Fisher #CTT11436)]

30. Tube cleaners, size A (Fisher #3-642)
31. Tubing, bubble, Argyle universal, plain, lumen 3/16 inch bore (Aloe Scientific #AR-500)
32. Tubing, rubber, red, thin wall, 3/16 inch bore (Fisher #14-166)
33. Tubing, Tygon, 1/4 inch I. D., 3/8 inch O. D., 1/16 inch wall
34. Washers, Milligan gas, two, (Fisher #7-513)
35. Yardstick

Preparation

Filling the combustion tube

Considerable care must be exercised in filling the combustion tube. The gaseous combustion products diffusing through the tube must come in contact with large surface areas, but the materials must not be so compact that the gas pressure heads will not afford the desired gas velocities through the tube. The following procedure is recommended (see Fig. 3 and section III, Reagents):

a) Twist several strands (ten to fifteen, 6-8 inches long) of silver wire together and insert into the tapered end of the combustion tube, occupies approximately 2 inches of the tube.
b) Hold the tube in a vertical position, i. e., with the tapered end down.
c) Add approximately one hundred grams of lead dioxide to the tube. The layer should be 4 inches in depth (yardstick may be helpful).
d) Insert ten grams of silver wool to form a 1/2-inch layer.

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a) Twist several strands (ten to fifteen, 6-8 inches long) of silver wire together and insert into the tapered end of the combustion tube, occupies approximately 2 inches of the tube.
b) Hold the tube in a vertical position, i. e., with the tapered end down.
c) Add approximately one hundred grams of lead dioxide to the tube. The layer should be 4 inches in depth (yardstick may be helpful).
d) Insert ten grams of silver wool to form a 1/2-inch layer.

e) Add approximately fifty grams of lead chromate to form a 2-inch layer (mix in a small amount of asbestos to help prevent caking).

f) Insert asbestos loosely to form a 3/4-inch plug.

g) Add approximately five hundred grams of cupric oxide to form a 9-inch layer.

h) Insert asbestos loosely to form a 1/2-inch plug.

i) Add approximately thirty-seven grams of lead chromate to form a 1-1/2-inch layer.(again mix in a small amount of asbestos)

j) Add the special mixture consisting of 20 ml of platinized asbestos plus 20 ml of asbestos plus 10 ml of aluminum oxide (approx. unpacked volume measurements). The layer should be 1-1/2 inch in-depth.

Assembling the combustion train

The components of the apparatus are assembled in the following sequence:

a) Oxygen cylinder with attached regulator which will afford a delivery pressure of 10 (p.s.i.g.)

b) Hard rubber stopcock, "on-off" valve

c) Erlenmeyer flask, 500 ml, with 2-hole, size #7, stopper (serves as a liquid-backflow trap)

d) Gas washer, containing 150 ml concentrated sulfuric acid

e) Drying jar: Magnesium perchlorate is placed in the lower half and ascarite, topped with activated alumina, in the upper half. A small layer of glass wool is inserted beneath the magnesium perchlorate and above the activated alumina. The oxygen flow into the jar is through the bottom inlet.

f) Rotameter, with the stainless steel float at a level affording an oxygen flow of 250 cc/min.

g) Glass stopcock held by a utility clamp on a support stand

h) Combustion tube, with sample inserter and oxygen baffle attached at the non-tapered end; a position mark, etched on the outside of tube 2-1/2 inches from the non-tapered end, enables the analyst to keep the tube in correct position within the furnace units, Aluminum foil is placed around the tapered end of the tube to maintain heat inside the tube and prevent water vapor from condensing.

i) Two Stetser-Norton bulbs (for water absorption), set up in series: each contains magnesium perchlorate between two loose layers of glass wool.

j) Two Nesbitt bulbs (for carbon dioxide absorption), assembled in series: a 1/2-inch layer of glass wool is placed in the bottom of the bulb. Indicarb® is then added to a point, 3/4 inch from the shoulder of the bulb. The Indicarb® is covered by a 1/4-inch layer of activated alumina. Introduce sufficient glass wool to reach the neck area and cotton in hollow stopper. (Note: For highly combustible materials or materials with high carbon content more than two Nesbitt bulbs may be necessary.)

k) Erlenmeyer flask, 500 ml, with 2-hole, size #7 stopper (serves as a liquid-backflow trap).

l) Gas washer, containing 150 ml barium hydroxidethymolphthalein solution.

m) Tygon tubing as connections between the oxygen cylinder, stopcock, erlenmeyer flask, gas washer and drying jar

n) Argyle tubing, used between drying jar, rotameter, glass stopcock, and the sample inserter

o) Rubber tubing, between the tapered end of the combustion tube, absorption bulbs, second erlenmeyer flask trap, and final gas washer.

Conditioning the combustion tube

A freshly packed tube contains excess moisture and must be dried out for 2 hours as directed in step no. 1 of the following "Procedure". After the 2 hour period, the analyst continues with the remaining procedural steps.

If the combustion tube has been previously used but has remained idle for more than one day, the analyst conditions the tube by performing only steps 2 and 3. During this idle period the glass stopcock must be turned so that nothing can flow into the combustion tube. The rubber stopcock is likewise closed so that the sulfuric acid does not flow from the gas washer back into the trap.

If the stopcocks are at their proper "shut-down" positions, no conditioning of the combustion tube is necessary with an idle period of one day or less.

A conditioned combustion tube in continuous use should last about six months or about 700 analyses. A close estimate of the life span for a conditioned tube is impossible to determine because of the variation in the samples' impurities and carbon-hydrogen concentrations.

Note: Before performing the following conditioning procedure, review the start-up and shut-down procedures.

Procedure	Comments
1. With the 8-inch furnace at 950C ± 20C (control level about 8.9) the 12-inch furnace at 800C ± 20C (about 4.5), and the 4-inch furnace at 200C ± 10C (about 2.0), allow oxygen to flow through the combustion train at 250 cc/min., with the rubber and glass stopcocks open. (Do not connect absorption bulbs) NOTICE: For newly packed tubes wait 2 hours before starting the next step.	1. a) Putting the 8-inch and the 12-inch furnaces temperature knob on "high" and the 4-inch furnace on "3" will allow the heat-up time to be about only 35 min. b) CAUTION: Never allow the temperature of the 8-inch furnace to exceed 1000C, the 12-inch furnace to exceed 840C, and the 4-inch furnace to exceed 220C. c) The stainless steel float in the rotameter should be approx. at the 8.2 cm level.

(Setting established for oxygen gas.

2. Follow the procedure outlined for analyzing samples except using 0.2 to 0.5 g of A.C.S. grade sucrose without a combustion aid.

2.a) Sucrose must be previously dried at 110C for one hour.

b) See "Analysis."

c) CAUTION: Higher weights of sucrose combust too violently.

3. Repeat step 2 above if observed carbon and hydrogen contents do not agree with theoretical values.

3. This step is usually necessary only with a freshly packed tube.

REAGENTS

All reagents are of ACS analytical reagent-grade quality. All solutions are prepared using distilled or deionized water. Reagents are as follows:

1. Oxygen, 99.5 percent pure (the oxygen should be prepared from liquid air. Oxygen, prepared by electrolysis, contains traces of hydrogen.)
2. Sulfuric acid, concentrated.
3. Dehydrite (anhydrous magnesium perchlorate).
4. Ascarite (sodium hydroxide in asbestos), 8-20 mesh.
5. Activated alumina, indicating, 8-14 mesh (Fisher #A-545).
6. Silver wire, 34 B & S gauge, pure grade (Fisher #20-272)
7. Lead dioxide, brown, 12-20 mesh.

8. Silver wool.
9. Lead, chromate, 12-20 mesh; or powder which was fused at 820C for one hour and ground to about 12-20 mesh.
10. Asbestos, medium or long fiber, acid washed.
11. Cupric oxide, black wire; before using, ignite at 800C for one hour.
12. Platinized asbestos, 5 percent (Fisher #P-152).
13. Aluminum oxide, anhydrous.
14. Accelerator chips, Combax (iron)(Fisher #C-420).
15. Indicarb®, 6-10 mesh (Fisher #1-181).
16. Absorbent cotton.
17. Glass wool.
18. Stopcock grease, Kel-F 90 (Fisher #14-635-10).
19. Barium hydroxide solution: dissolve 12.0 g $Ba(OH)_2$ in distilled water and dilute with same to one liter.
20. Thymolphthalein solution: dissolve 10.0 g thymolphthalein in ethanol dilute with same to one liter.
21. Barium hydroxide - thymolphthalein solution: add 0.5 ml of the thymolphthalein solution to 150 ml of the barium hydroxide solution.

SAFETY PRECAUTIONS

A wooden safety shield 2 x 2 x 3/8 inch, or the equivalent, should be placed about three feet from the right side of the furnace base, such that, if the rubber stopper with the sample inserter should blow out, the stopper and inserter will hit the shield.

The sample boats should never be inserted faster than the prescribed one inch each 5 minutes, after the initial 5 minute wait, for the first 20 minutes of total insertion time. Faster sample insertions may cause the above mentioned blow out or a more violent explosion. If the sample ignition is too violent, the analyst should divert the oxygen flow by turning the glass stopcock and allowing the oxygen to flow into the room.

Normally the oxygen flow rate is reduced during the initial ignition, which generally occurs upon the first or second one-inch insertion, and should not be adjusted during this period. The flow rate of 250 cc/min. is sufficient to prevent the back flow of gases into the rotameter. Always keeping the sample inserter's blunt end, while in initial position, approx. 1/4 inch away from baffle will help maintain the oxygen flow.

If the exit gas flow-stops, the oxygen inlet flow is immediately turned off by using the glass stopcock, as mentioned above. This gas flow stoppage may be due to an unopened absorption bulb or too tight tube compaction.

The analyst should always be aware of the hot boats, the hot furnace parts, and the general bubble flow rate in the exit gas washer. He should not remain close to the combustion tube during the sample's initial ignition because explosions are anticipated mostly at this time.

SAMPLE PREPARATION

The details of sample preparation procedures which describe the drying and grinding techniques are not discussed in this laboratory procedural report. In general, raw refuse, residue (organics), and compost are dried at 70C to a constant weight and ground to a particle size of less than 1 to 2 mm. Residue (fines) and fly ash samples

are dried at 105C to a constant weight and pulverized to pass through a #60 sieve.

All samples must be redried no more than one week before being weighed for the analyses. The procedures for this redrying are 1) those samples which were originally dried at 70C must be redried at 70C for four hours; and 2) those samples originally dried at 105C must be redried at 105C for one hour. After redrying procedures, all samples must be kept in tightly closed containers and in a desiccator until the analyses are performed.

PROCEDURE

Start-up

The "start up" procedure for the carbon-hydrogen analyses is always the same, except for a freshly packed tube as previously mentioned. The following procedure outlines the routine steps in preparing the carbon-hydrogen train for the analyses.

Procedure	Comments
1. Set the temperature controls of the 8-inch and 12-inch furnaces on "high" and the 4-inch furnace on "3" for about 35 minutes. Final temperatures for the 8, 12, and 4-inch furnaces are 950C ± 20C, 800C ± 20C, and 200C ± 10C, respectively.	1. CAUTION: Never allow the temperature of the 8-inch furnace to exceed 1000°C, the 12-inch furnace to exceed 840°C, and the 4-inch furnace to exceed 220°C.

2. After each furnace has reached its appropriate temperature, set the 8-inch furnace control on "8.9", the 12-inch furnace control on "4.5", and the 4-inch furnace control on "2.0."

2. These numbers are not absolute and may change with the age of the elements.

3. Open the rubber stopcock and without much delay allow the oxygen to flow through at approximately 250 cc/min. The delivery pressure gauge is set at 10 (p.s.i.g.). Flow adjustments are made with the needle-valve control.

3.a) The glass stopcock should be open to the room.

b) If the oxygen is not soon allowed to flow, sulfuric acid will flow back into the trap.

c) The stainless steel float in the rotameter should set and maintained at approximately the 8.2 cm level.

4. Turn the glass stopcock to allow oxygen to flow through the combustion tube.

4.a) If the float drops drastically toward the zero level, immediately return glass stopcock to its former position. Then the charger-rake rod may be used to loosen the tube packing.

b) Absorption bulbs should not be attached.

5. Attach at least two of each type of absorption bulbs and again notice the stainless steel float and bubbles in the exit gas washer.

5.a) The bubble flow rate in the exit gas washer is a good indication as to how the oxygen is flowing through the train. If the bubbles do not start, an absorption bulb may be closed or packed too tightly.

b) If the samples to be analyzed are known or suspected to contain more than 30% carbon and if sample weights of more than 1.5g are used, attach three or more absorption bulbs for the CO_2 collection.

6. Adjust the oxygen flow to be approximately 250 cc/min.; the stainless steel float should be at the 8.2 cm level.

6. The flat end of the sample inserter should always be slightly away from the end of the baffle to allow the free flow of oxygen.

7. With the train completely assembled, allow the oxygen to flow through the system for 10 min.

7. This insures the conditioning of the absorption bulbs.

8. Remove the absorption bulbs from the train and close each bulb to the atmosphere.

9. Determine and record the weight of each CO_2-absorbing bulb and each H_2O-absorbing bulb. These weights represent the initial weights of the absorption bulbs.

9.a) The bulbs should be near room temperature before being weighed. Normally each bulb will be near room temperature, if the order of weighing is started with the last bulb in the train.

b) Before weighing, each bulb is momentarily vented to the atmosphere and wiped clean with a lint-free cloth.

c) Use an analytical balance with a 200 gram capacity and 0.1 mg readability.

d) Weights are recorded to the nearest 0.0001 gram.

10. After opening the absorption bulbs to permit gas flow, quickly return the bulbs to the train assembly.

10) Start with the bulb furthest from the furnace. The connection of the bulbs to the furnace should be performed last.

11. When the gas starts through the exit gas washer the train is ready for sample analyses.

11) If the gas does not start through the exit gas washer, check bulbs openings and compaction of absorbing materials.

Blanks

Increase in weight of the absorption bulbs is due to 1) sample ignition, 2) sample container's contamination, 3) atmospheric contamination during sample insertion, and 4) impure oxygen gas. The blank analyses determine the affects of all the above factors, except sample ignition, upon the weights of absorption bulbs. These blank analyses are conducted as the regular sample analyses except pre-ignited empty sample containers with covers and an unpacked combustion tube are employed. The unpacked tube is needed for the blank analyses because lead dioxide is high hygroscopic.

The analyst is advised to perform triplicate observations and record the humidity (may be estimated) of the room during the analyses. Whenever the oxygen supply is changed or the room humidity greatly changes the blank analysis should be repeated. The carbon dioxide blank value is usually zero and the water blank value normally varies with analysts.

Standards

After conditioning the combustion tube as previously described, the analyst should periodically check the carbon-hydrogen train by analyzing standards, such as sucrose, naphthol, urea, graphite, calcium carbonate, and solid wastes samples which have been previously analyzed. The procedure for analyzing standards is the same as described for sample analyses. However, analyze only 0.2 to 0.5 grams of sucrose and without a combustion aid since this standard burns

quickly and easily. Benzoic acid, although commonly used as a carbon standard, reacts too violently for this method.

Samples

At this point, all the necessary conditioning should have been performed so that the carbon-hydrogen train is now ready for sample analyses. The following procedure applies to all solid waste materials, also to blanks and standards with the previously mentioned changes. All the sample containers and covers employed in the method must have been previously ignited at 950C for one hour, then cooled and stored in a desiccator until used.

The analyst is advised to analyze samples of each particular type of solid waste materials as a unit. Switching back and forth between different types of materials, which usually vary greatly in their carbon-hydrogen content, causes unnecessary reconditioning and re-checking of the combustion tube. To insure good results, the analyst should always analyze a standard before analyzing a particular type of solid waste material. This standard should be of the same general character as the type of material to be analyzed.

A combustion aid must be mixed with each sample after the sample has been weighed into its container. Some samples combust vigorously and the sample injection procedure may have to be slowed down; however, even vigorously reacting samples need a combustion aid.

The analyst must use his own judgment in the selection of the sample container, the number of absorption bulbs in the train, the unscheduled removal of an absorption bulb, and the change of the sample insertion procedure.

Procedure	Comments
1. Transfer, at least, one to two grams of a sample into each of two previously weighed combustion boats. Determine and record the weight of each sample to the nearest 0.0001g.	1.a) Sample weights up to ten grams may be used, if non-uniformity of sample warrants. b) Fluffy samples, such as compost samples, require the larger containers. c) Minimize handling of boats and lids to prevent contamination. d) Keeping the boats in a particular order or numbering them will prevent mix-up of samples. e) DO NOT pelletize any sample. If a one to two-gram sample will not fit into a particular boat use a larger container.
2. Sparsly sprinkle each sample with a small amount of iron chips. Using a spatula, mix the combustion aid throughout the sample.	2.a) Granular tin (Fisher #12-173) may be used as an accelerator, if iron chips are not available. b) REMINDER: <u>DO NOT</u> use a combustion aid with sucrose.

3. Store each boat, containing a sample, with its lid in a desiccator until they are transferred to the combustion tube.

3.a) It is convenient to use a stiff asbestos pad to support the boats while in the desiccator and during transfer from one place to another.

b) The desiccator must contain CO_2 absorbing and H_2O-absorbing materials.

4. Cover each boat with its lid and transfer them from the desiccator to insertion end of combustion tube. Immediately, go to the next step.

4. REMINDER: Flat end of sample inserter must be slightly away from the baffle to permit free flow of oxygen.

5. Remove stopper with attached sample inserter and place boat about half way into tube. Then close the combustion tube by moving the sample inserter, with baffle, along the bottom of the tube; holding the tube with the left hand, twist the stopper tightly into the tube. Immediately go to next step.

5.a) Do this step quickly. The blank value will only be applicable if the time required for placing the boat in the combustion tube is constant.

b) If the combustion tube contains the boat and lid from the previous sample analyses, use the charger-rake to remove the boat and lid onto a stiff asbestos pad. Then drop the boat and lid into an enameled pan which is lined with asbestos pads. After they have cooled the boat and lid are transferred to a stainless

steel pan, cleaned, and finally ignited at 950C for one hour before being reused.

6. Upon closing the combustion tube, set a timer for 60 minutes. Check the flow rate to see if it is 250 cc/min. (stainless steel float at 8.2 cm level), after the gases are bubbling through the exit gas washer.

6.a) The stainless steel float will drop momentarily and adjustment is needed if it remains below the 7.1 cm level more than a few moments. However, DO NOT attempt to adjust the flow rate if the sample ignition has started. Except when using the large clay boats, sample ignition usually starts after the sample is closer to the 950C zone.

b) REMINDER: Safety-Caution. If bubbles in exit gas washer stop completely for more than 5 to 10 minutes and the stainless steel float begins dropping (caused by too vigorous sample combustion), turn the glass stopcock, thus diverting the oxygen from the combustion tube to the room. Whenever the stopcock must be turned, the results of the particular test must be discarded.

7. After 5 minutes, move the sample boat one inch toward the 950C zone.

7. If the sample has already ignited vigorously, delay this step for another 5 minutes.

8. At the end of each of 3 successive 5-minute intervals move the sample boat one inch toward the 950C zone.

8.a) DO NOT move the sample boat at a faster rate, even if one of the one-inch insertion step was forgotten. However, after some experience the analyst may accelerate the insertion procedure when analyzing residue (fines) or fly ash samples.

b) During this step, the Indicarb® may indicate that another tared absorption bulb should be added.

9. After another 5 minutes, move the sample boat completely into the middle of the 950C zone.

9.a) The entire period of sample insertion should not exceed 30 minutes.

b) If the large clay boats were employed, most of the boat will be beyond the center of the 950C zone.

10. Allow the oxygen to flow through the train for the rest of the 60-minute period.

11. Remove the absorption bulbs from the train and close each bulb to the atmosphere.	11. The oxygen continues to flow through the combustion tube while the absorption bulbs are removed. However, if more than 30 minutes will elapse before another sample is started the oxygen flow must be diverted away from the combustion and into the room by turning the glass stopcock.
12. Determine and record the weight of each CO_2-absorbing bulb and each H_2O-absorbing bulb.	12.a) This weight represents the final weight of each absorption bulb and is used as the initial weight of each bulb for the next sample. b) The time required for weighing should not exceed 15 minutes.
13. Return the sample inserter to "start" position.	13. When the flat end of the sample inserter is slightly away from the baffle, thus permitting a free flow of oxygen through the baffle, the sample inserter is in the "start" position.
14. If another sample, contained within a boat, is ready to be analyzed, repeat the procedure starting with step #4.	

15. If the train is not to be used for more than 1/2 hour, see "Shut-Down" procedure.

Shut-Down

As mentioned under "Conditioning the combustion tube" the proper "shut-down" procedure prevents the necessity for reconditioning the combustion tube. If the train is not used for more than 1/2 hour and the oxygen is allowed to flow through the combustion tube, the packing materials, especially the lead dioxide, will dry out and require reconditioning before the train can be employed again. If the train is to be used the same day but not for more than 1/2 hour, the furnaces temperatures may be maintained but the oxygen flow must be diverted from flowing through the combustion tube or shut off completely. Whenever the oxygen flow is shut off the glass and rubber stopcocks must be closed as described below.

Procedure	Comments
1. Disconnect the absorption bulbs from the combustion tube and close each one to the atmosphere.	1. Any remaining boat and lid should be removed from the combustion tube.
2. Having the combustion tube stoppered and the sample inserter in "start" position, turn each furnace "off".	2. Furnaces need not be turned "off" if used later the same day.
3. Turn "off" the oxygen flow first at the main regulator valve on the oxygen cylinder, then at the low	

pressure valve. Immediately go to the next step.

4. Turn the glass stopcock to divert any oxygen flow from the combustion tube to the room atmosphere. Immediately go to the next step.

5. Close the rubber stopcock.

5. When the rubber stopcock is closed the backflow of sulfuric acid into the trap is prevented.

CALCULATIONS

Standards

Formula

Employ the following formula to calculate the theoretical concentration of either carbon or hydrogen in a standard sample:

$$\% E = \frac{(N)(F)(100)}{(S)(P)}$$

Where % = the percent by weight

E = the element, either carbon or hydrogen

N = the number of atoms of the element in a molecule of the standard

F = a factor, derived by dividing the gram-atomic weight of the element by the gram-molecular weight of the standard

S = the weight of the total sample

P = the decimal fraction representing the concentration of the standard compound in the total analyzed sample (Note: this decimal

fraction is the only fraction containing the component being analyzed for).

Example

Pure Sucrose, $C_{12}H_{22}O_{11}$ (NBS Grade)

$$\%C = \frac{(12)[\overset{12.01}{342.30}](100)}{(1.0000)(1.00)} = 42.10$$

$$\%H = \frac{(22)[\overset{1.008}{342.30}](100)}{(1.0000)(1.00)} = 6.48$$

When the impurities listed on the bottle are considered, the calculated percents of carbon and hydrogen in ACS grade sucrose are 42.09 and 6.48 respectively.

Samples

Carbon

Employ the following formula to calculate the concentration of carbon in a solid wastes sample:

$$\%C = \frac{(A - B)(X)(100)}{(S)}$$

Where % = the percent by weight

C = the element carbon

A = the sum total increase in the weight of the CO_2-absorbing bulbs as determined in the unknown analysis

B = the sum total increase in the weight of the CO_2 absorbing bulbs as determined in the blank analyses

X = a factor, derived by dividing the gram-atomic weight of carbon by the gram-molecular weight of carbon dioxide; i.e., (12.01) ÷ (44.01) = 0.2729

S = the weight of the total sample

Hydrogen

Employ the following formula to calculate the concentration of hydrogen in a solid wastes sample:

$$\%H = \frac{(A - B(Y)(100)}{(S)}$$

Where % = the percent by weight

H = the element hydrogen

A = the sum total increase in the weight of the H_2O-absorbing bulbs as determined in the unknown analysis

B = the sum total increase in the weight of the H_2O-absorbing bulbs as determined in the blank analyses

Y = a factor, derived by dividing the gram-molecular weight of hydrogen by the gram-molecular weight of water; i.e., (2.016 ÷ (18.02) = 0.1119

S = the weight of the total sample

METHOD EVALUATION

The accuracy of this newly developed method was established (Table 1). This method can analyze solid wastes materials containing various forms of carbon to within one actual percent of the true value. For these tests, sucrose, naphthol, and urea were selected to represent hydrocarbons. Graphite was employed as elemental form of carbon and calcuim carbonate as an inorganic form. This method has accurately (100.00% recovery) analyzed specially prepared residue (fines) samples calculated to contain only 0.46 percent carbon and 0.01 percent hydrogen. This method should definitely not be employed to analyze samples which contain less than 0.1 percent carbon.

The precision of this method was determined by analyzing, in triplicate, a number of solid waste samples of various types. The pooled standard deviation of the observations for each type of solid wastes was calculated using an Olivetti Underwood Programma 101. The calculations revealed that, in the analyses of each type of wastes, the duplicate and triplicate determinations were equally precise (Table 2). To ensure good precision the particle size of the samples must be less than 2 mm or pass through a #60 sieve, then thoroughly mixed before analyzing.

With this macro method the analyst normally uses a one to two-gram sample, but he is not restricted to this amount. Because of the difficulties in preparing a very uniform sample, sample weights below one gram have been found inadequate when analyzing solid waste materials. But samples up to ten grams have been analyzed with no difficulty. The extra sample weights, however, add little to the precision of this method.

TABLE 1 - ACCURACY OF CARBON AND HYDROGEN DETERMINATIONS OF STANDARD COMPOUNDS

Compound	No. of Determ.	% Element Calcd.		% Element Found		% Recovery	
		C	H	C	H	C	H
Sucrose, NBS	6	42.10	6.48	42.07	6.39	99.93	98.61
Sucrose, ACS	6	42.09	6.48	42.02	6.39	99.83	98.61
1-Naphthol, ACS	3	83.31	5.59	82.72	5.86	99.29	104.83
Urea	3	19.99	6.71	19.38	6.66	96.95	99.25
Calcium Carbonate	3	11.97	--	12.04	--	100.58	--
Graphite[a]	3	83.28	--	84.01	--	100.88	--

[a]Since the graphite is not pure, the graphite, for this study, was ignited in air at 1150°C to determine the percent ash impurities.

TABLE 2 - STANDARD DEVIATION OF THE CARBON AND HYDROGEN DETERMINATION ON SUCROSE AND SOLID WASTES

Type of Sample	Number of Samples	Standard Deviation[a] Carbon Observations		Hydrogen Observations	
		Duplicates	Triplicates	Duplicates	Triplicates
Sucrose, NBS	2	--	0.17	--	0.15
Sucrose, ACS	2	--	0.15	--	0.19
Compost	26	--	0.29	--	0.10
Compost	56	0.22	--	0.14	--
Raw Garbage	17	0.18	0.19	0.19	0.18
Residue (fines)	16	0.04	0.06	0.04	0.03
Residue (organics)	8	0.21	0.23	0.22	0.18
Fly Ash	9	0.04	0.08	0.06	0.04

[a]A variance estimate can be calculated from the duplicate (or triplicate) set of observations for each sample. The pooled variance is essentially an average of all such estimates for samples of a given type. It is assumed that a single underlying variance exists for all samples of a given type. The pooled variance is then the best estimate of this underlying variance. The pooled standard deviation is the square root of the pooled variance and is used to estimate the underlying standard deviation.

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